Experimental and Theoretical Studies of Carbon Nanotube Hierarchical Structures in Multifunctional Hybrid Composites

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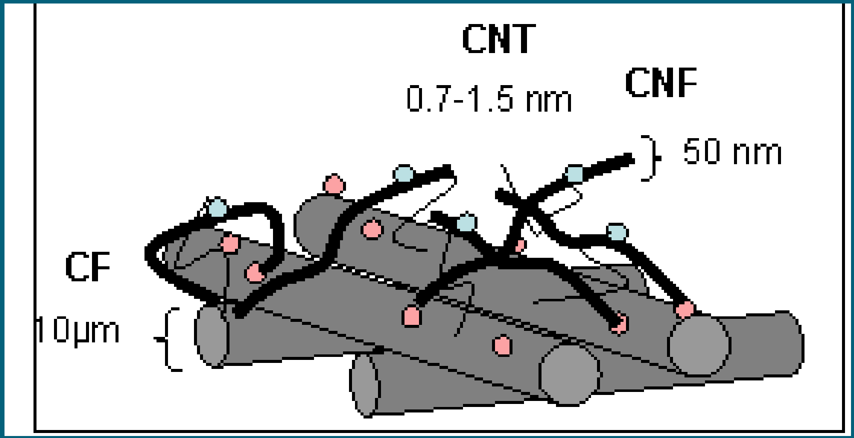
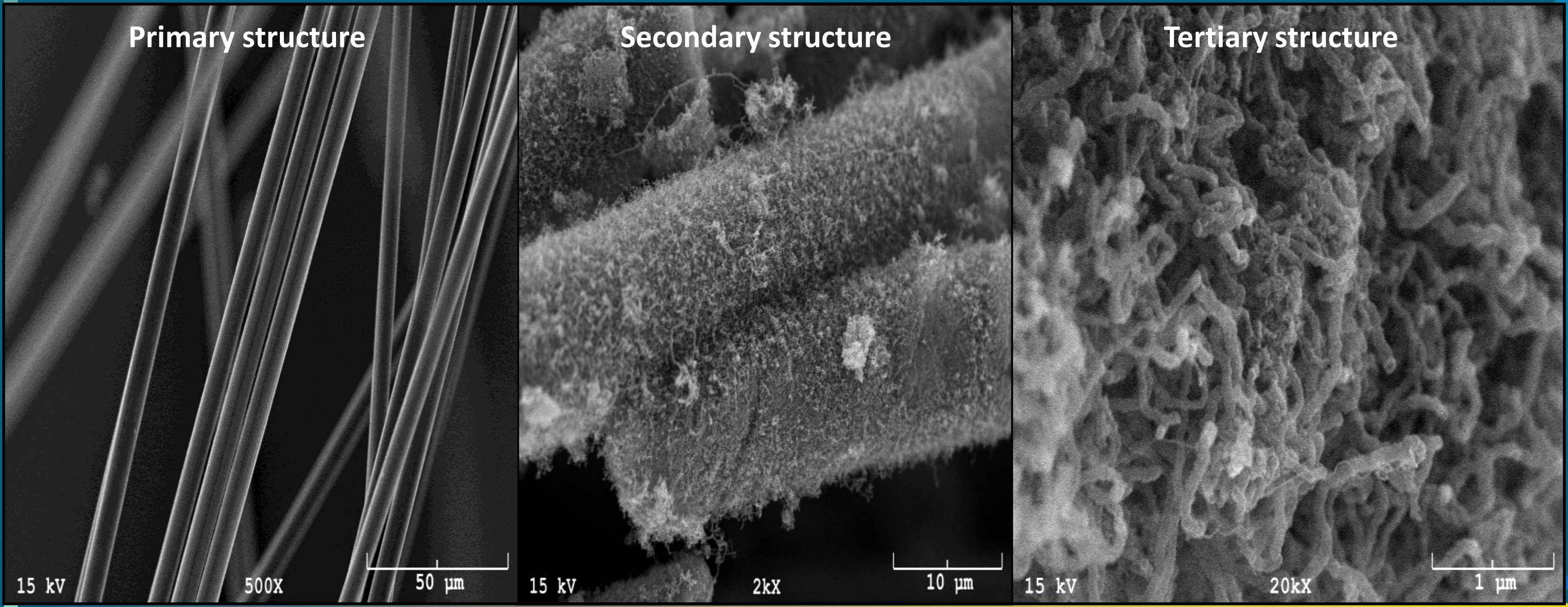
Introduction

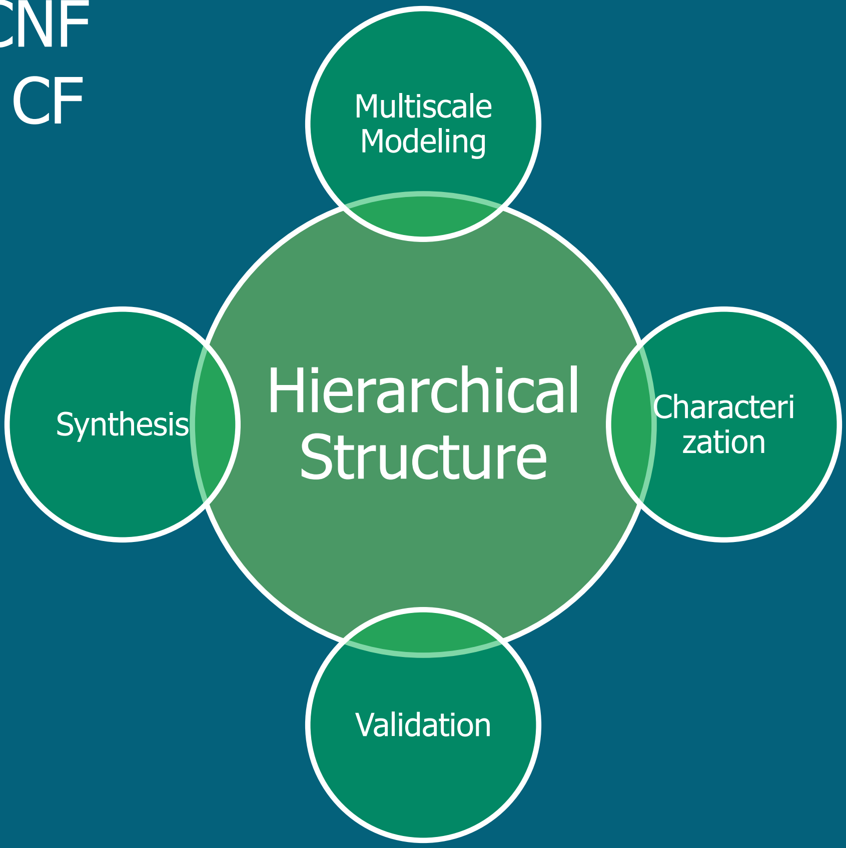
Nanoscale reinforcement is locally segregated at the microscopic scale with controlled orientation



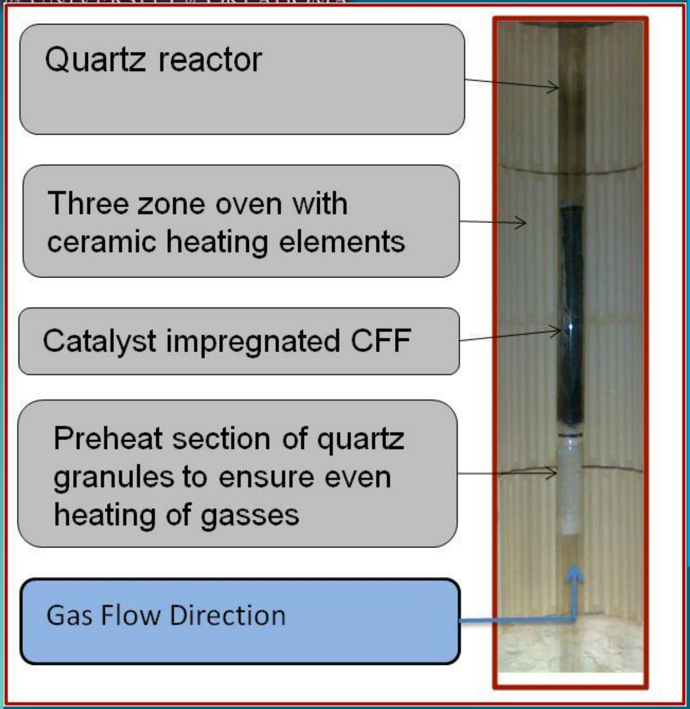


Objectives and Approaches

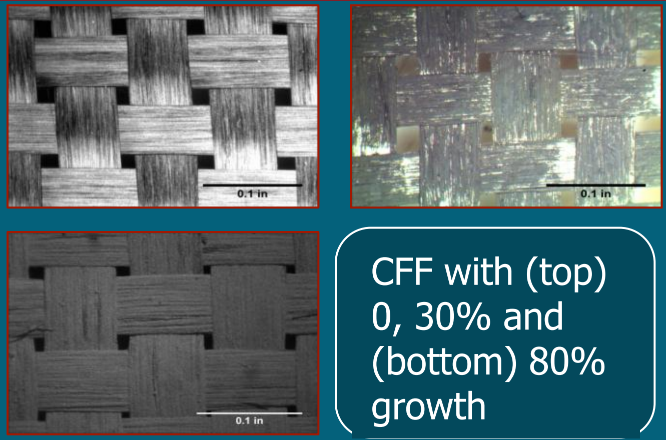
- Synthesis and investigate of the growth morphology of CNF and CNT nanostructures on CF
- Investigate the process parameters affecting nanostructure morphology
- Investigate the growth on mechanical properties and thermal conductivity
- Investigate heat transport behavior using multi-scale modeling approach



Synthesis of CNF on CF Using CVD

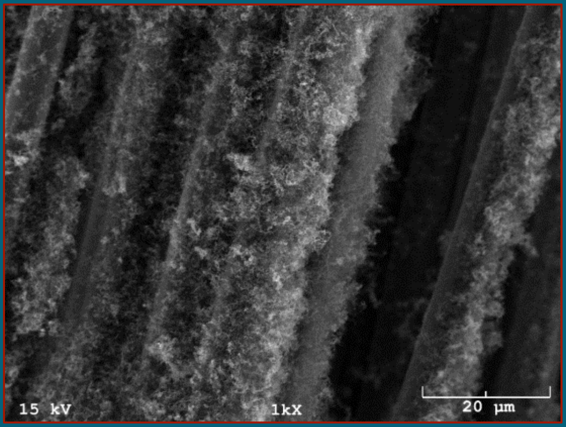


2.5″ x 6″ CF

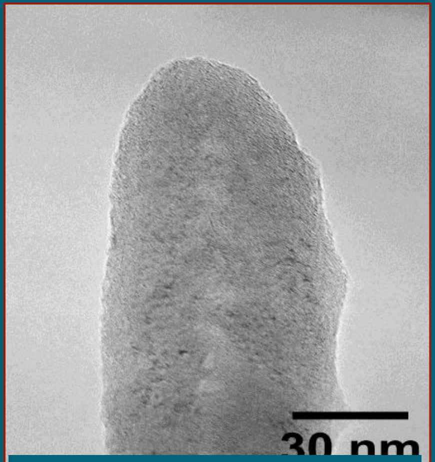


CFF with (top) 0, 30% and (bottom) 80% growth

- *Precursors:* $Cu(NO_3)_2$, $Ni(NO_3)_2$
- Cu:Ni= 1:9
- *Deposition: Ion exchange vs.* Spray
- *Calcination*: 300ºC for 1 hr in Air
- *Reduction:* 500ºC for 30 min in Hydrogen
- *Reaction* : 750ºC for 30 minutes in Ethylene

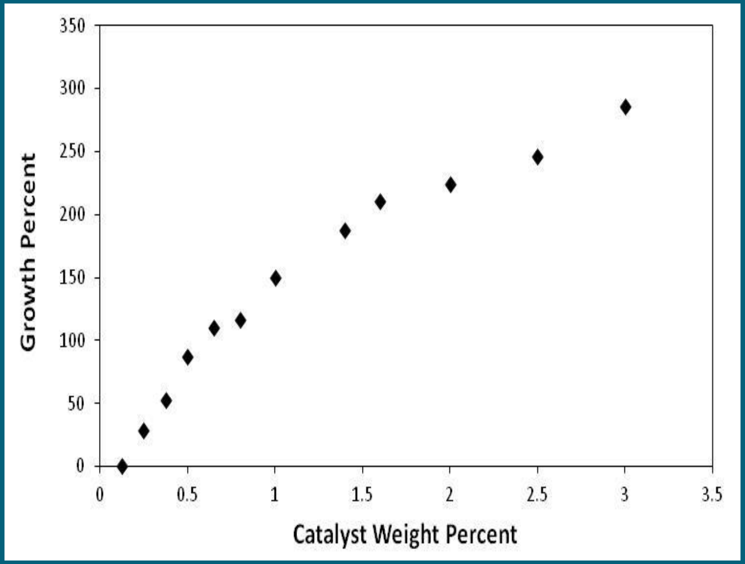


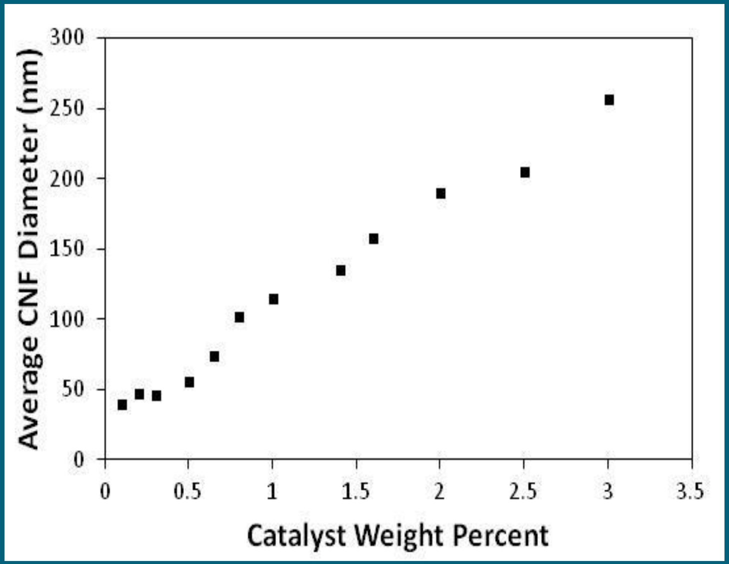
SEM showing CNF growth

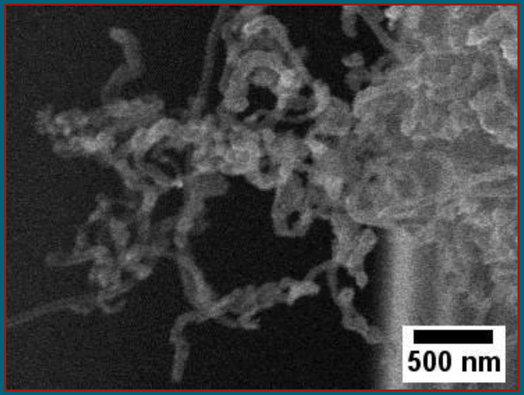


TEM confirms CNF

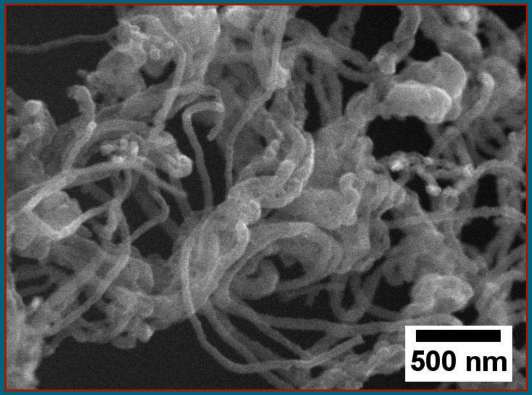
Catalyst Loading on CNF Growth



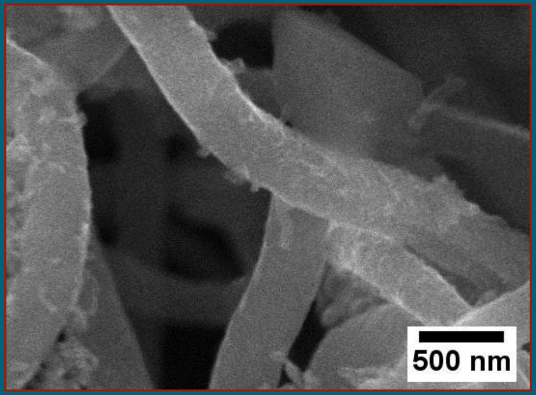




0.1 wt% catalyst

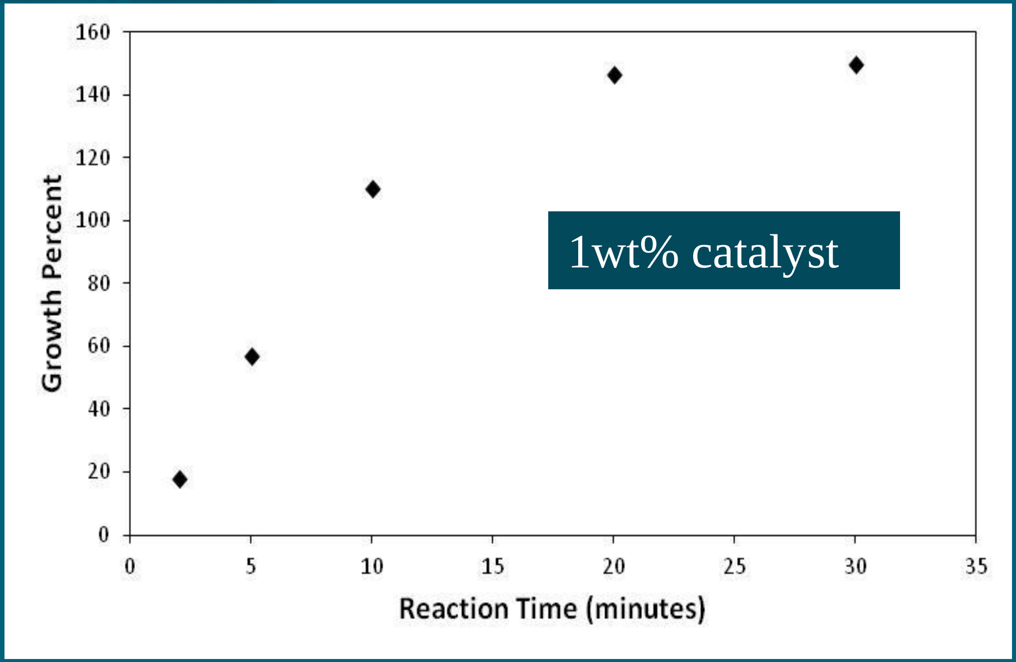


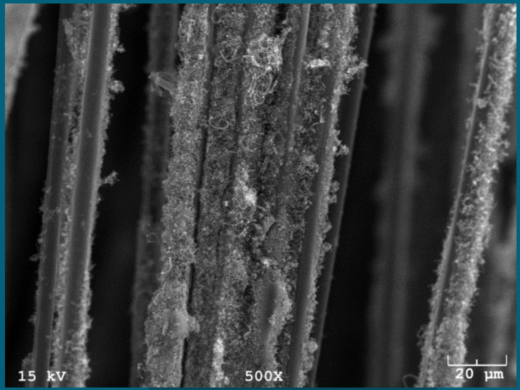
0.3 wt% catalyst



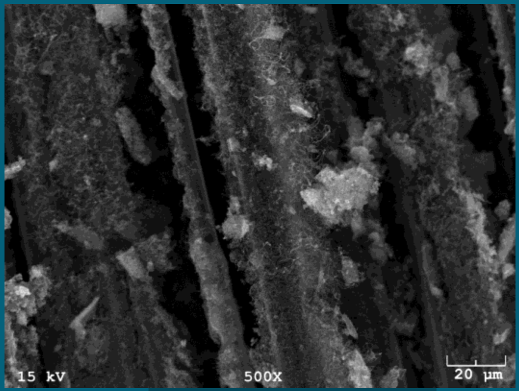
3.0 wt% catalyst

Reaction Time on CNF Growth

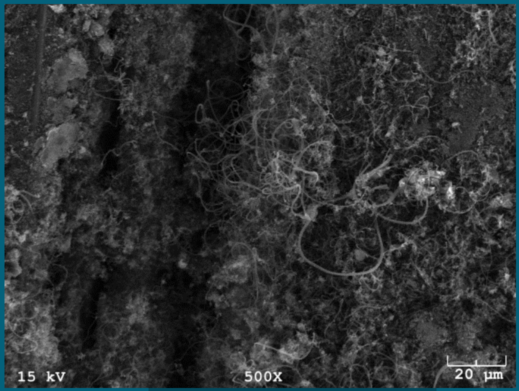




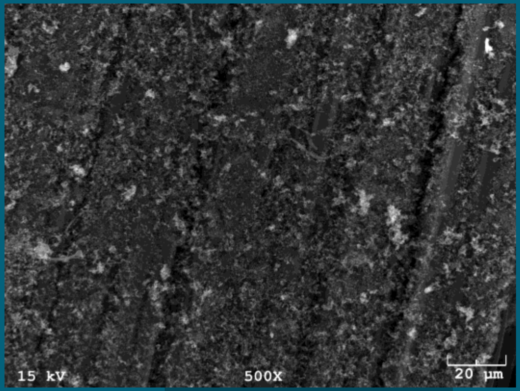
2.5, minutes



5 minutes

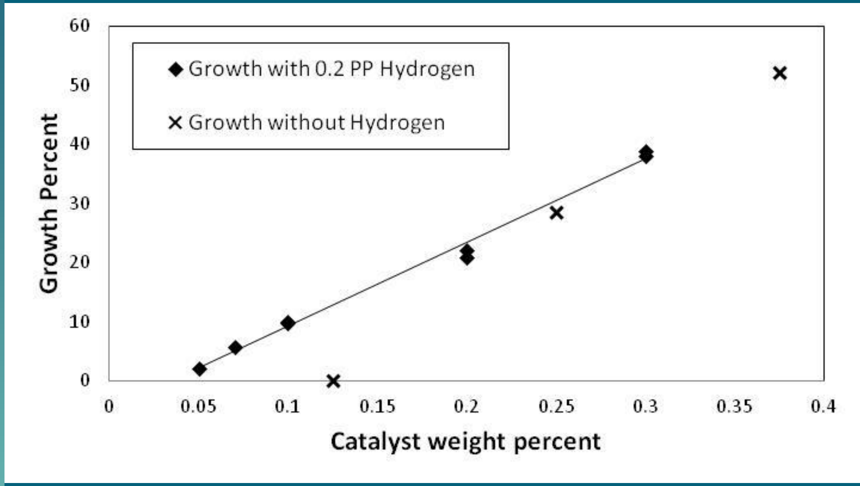


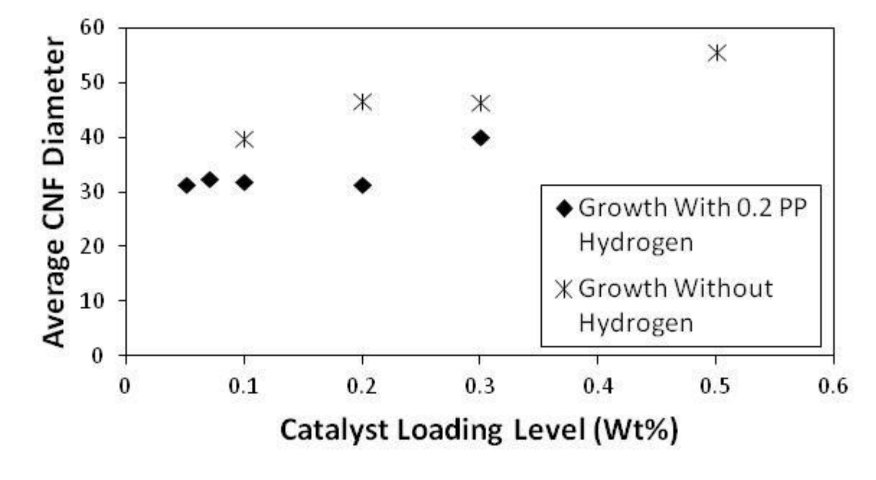
20 minutes

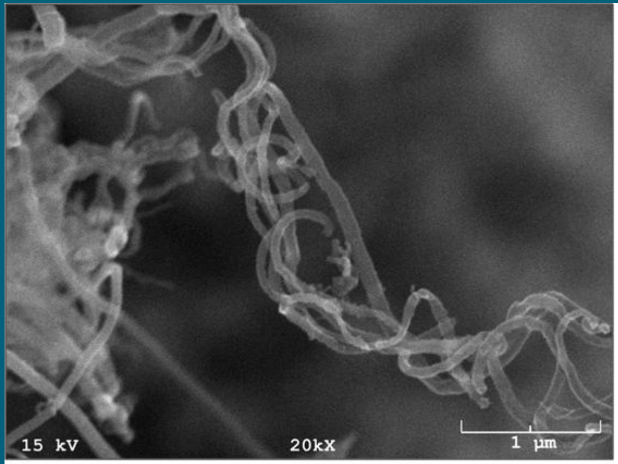


30minutes

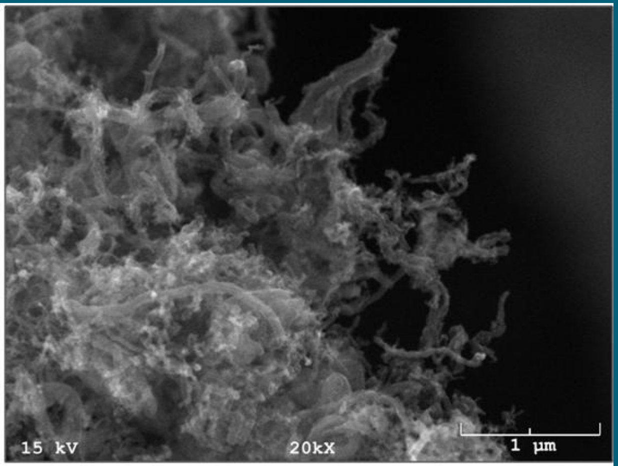
Hydrogen Dilution on CNF Growth







SEM image of growth from pure Ethylene

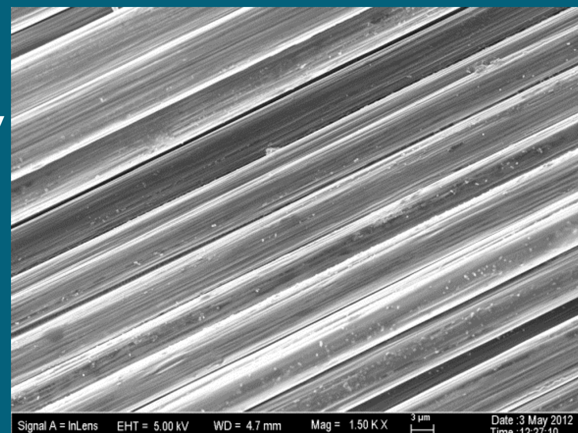


SEM image of growth from Ethylene/ Hydrogen mix

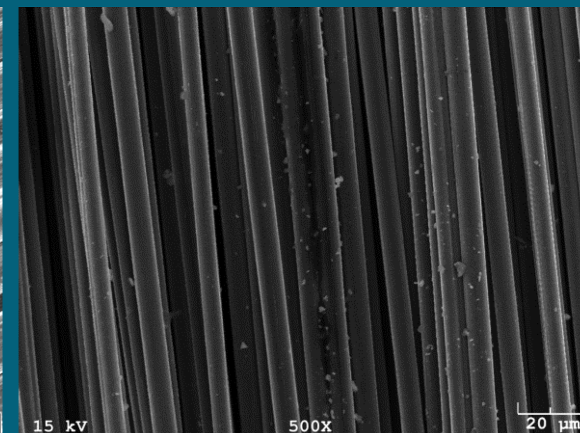
CVD of CNT Growth on CFs

SEM images at different stages of the growth process

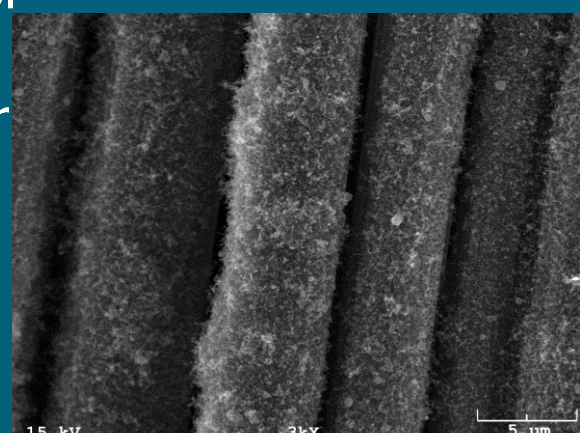
- *Precursors:* $Fe(NO_3)_3$, $(NH_4)_2MO_2O_7$
- Fe:MO= 2:1
- Hand Spray
- *Calcination* : 300°C for 1 hr in Air
- *Reduction :* 500°C for 30 min in Hydrogen
- *Reaction* : 750°C for 30 minutes in Ethylene



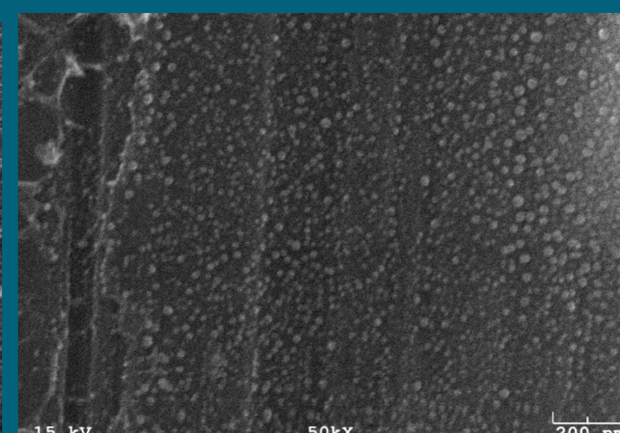
Before calcination



After calcination



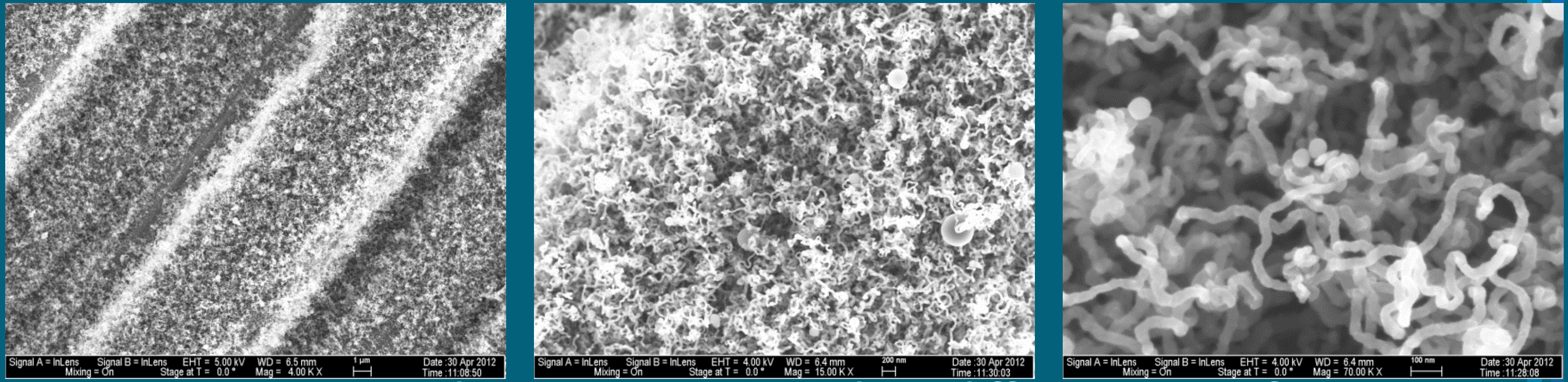
After growth



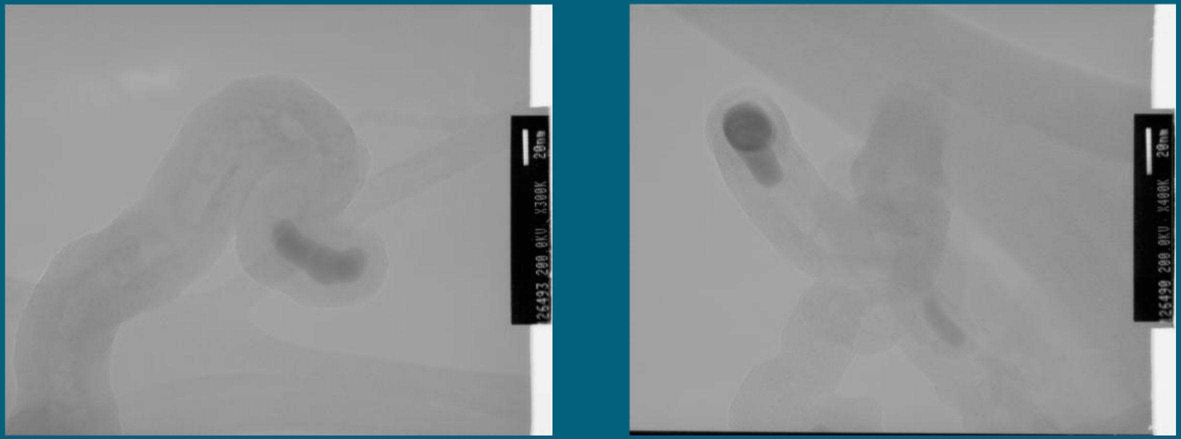
After reduction

CVD of CNT Growth on CFs

CNT growth performed at 750°C



SEM images showing CNTs growth at different magnification

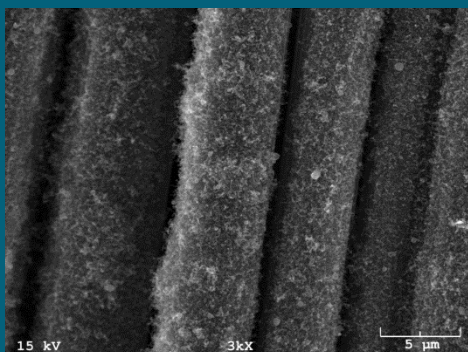


TEM images confirm CNTs structure with tip growth

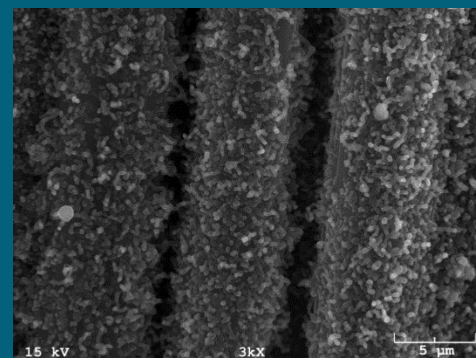
CVD of CNT Growth on CFs

Comparison of two methods of catalyst deposition

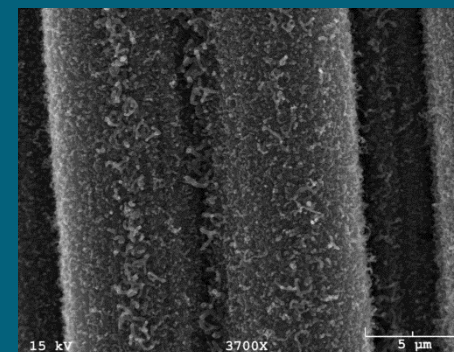
Spray



750°C

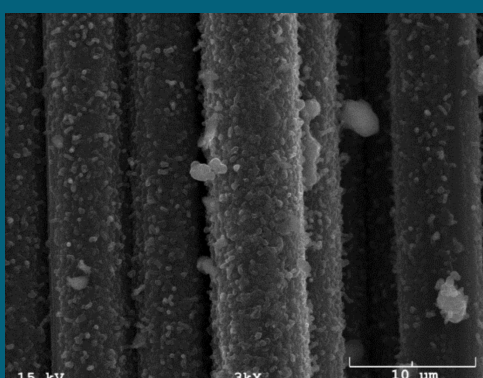


780°C

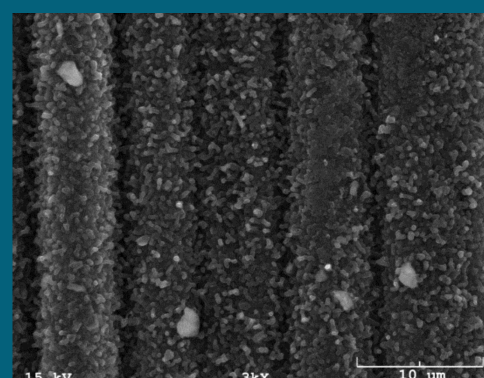


800°C

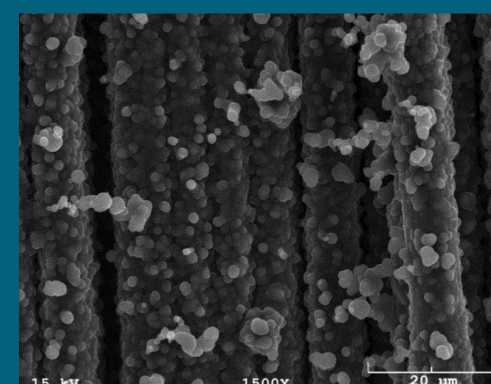
Ultrasonic Atomizer



750°C

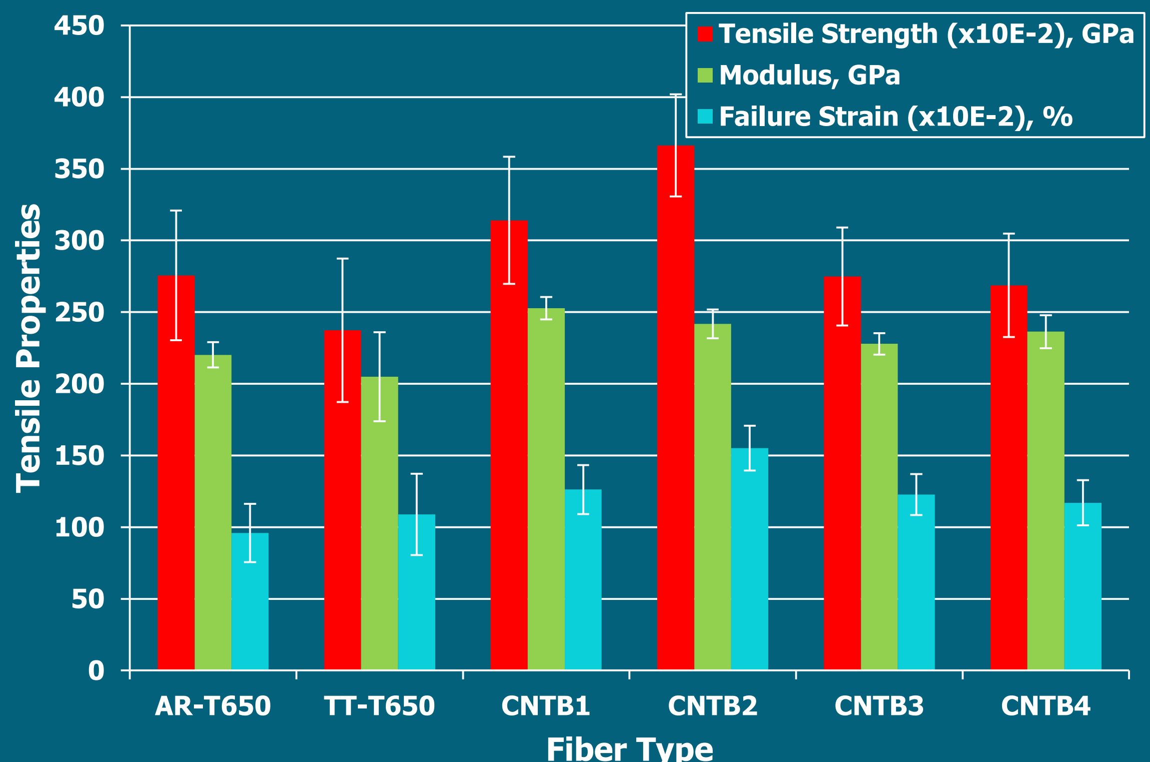


780°C



800°C

Effect of CNTs on Tensile Properties of Carbon Fiber



CNTB1- AR-Spray; CNTB2- AR—Dip
CNTB3- TT- Spray; CNTB4- TT-Dip

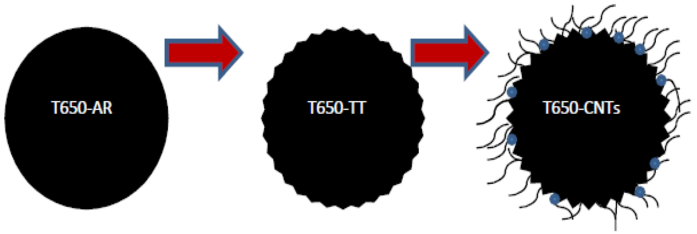
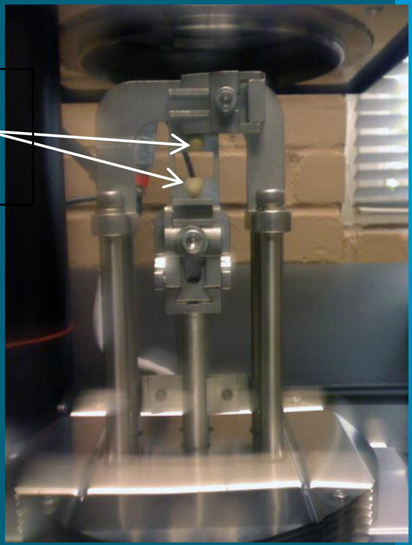


Illustration of fiber surface flaws/irregularities filled with catalyst metals and/or CNTs

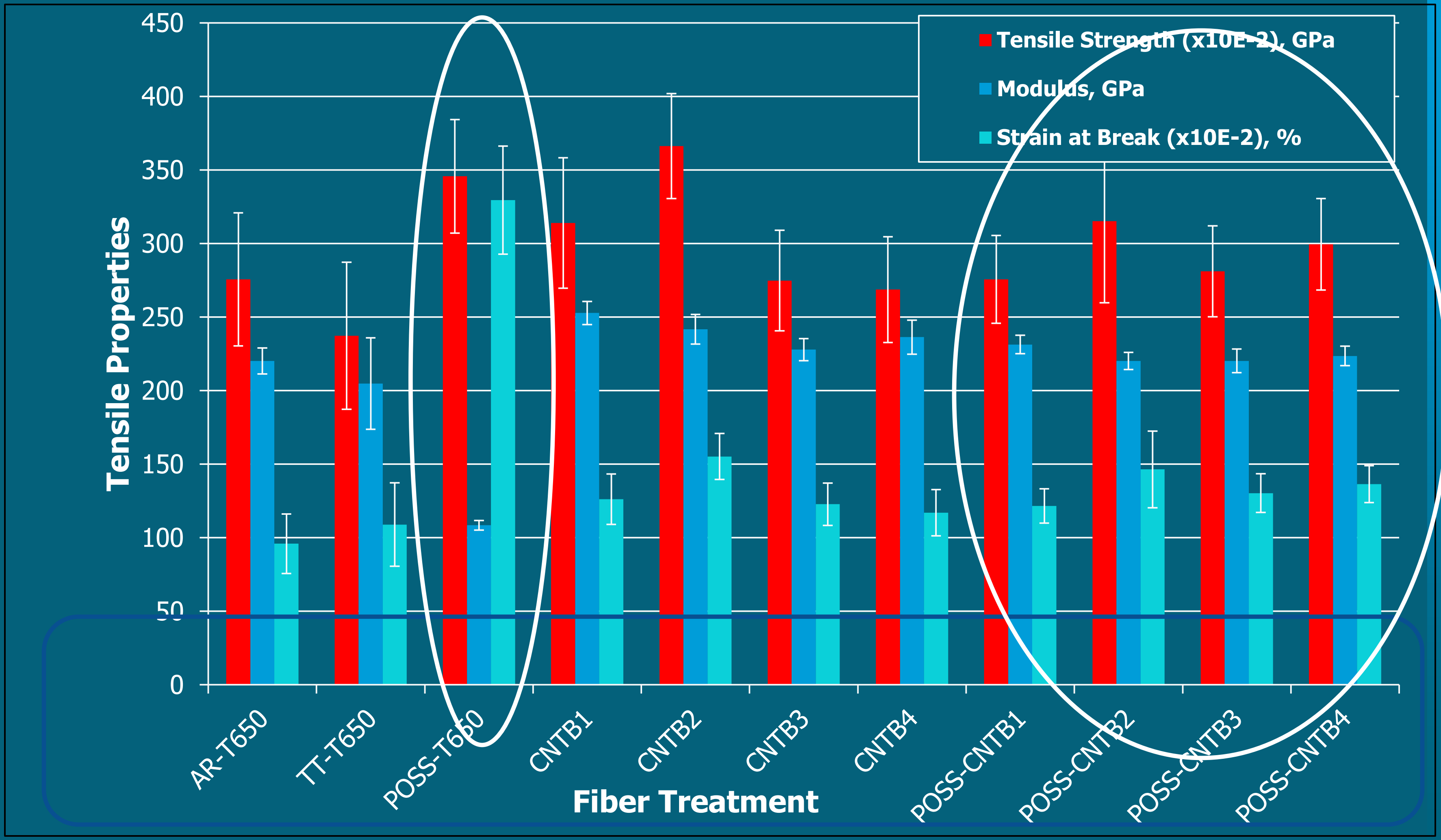
Bonded ends of the steel frame



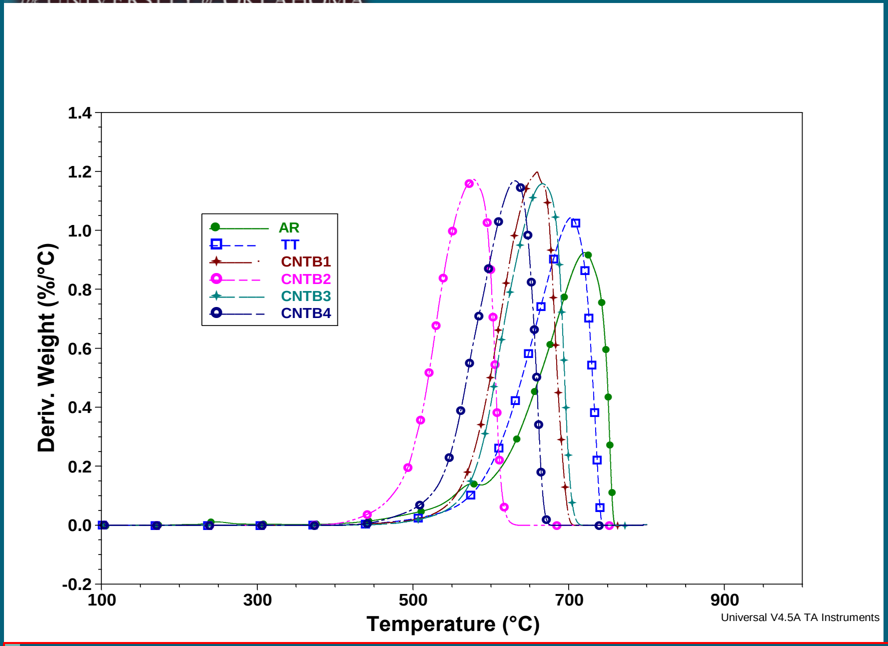
DMA Q800

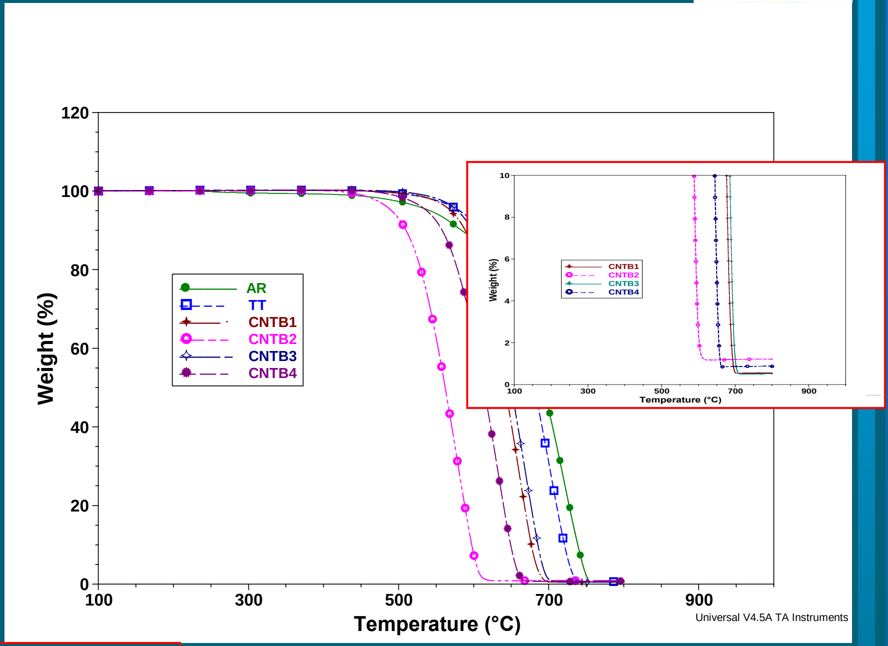
Steel shim frames used for mounting the fibers

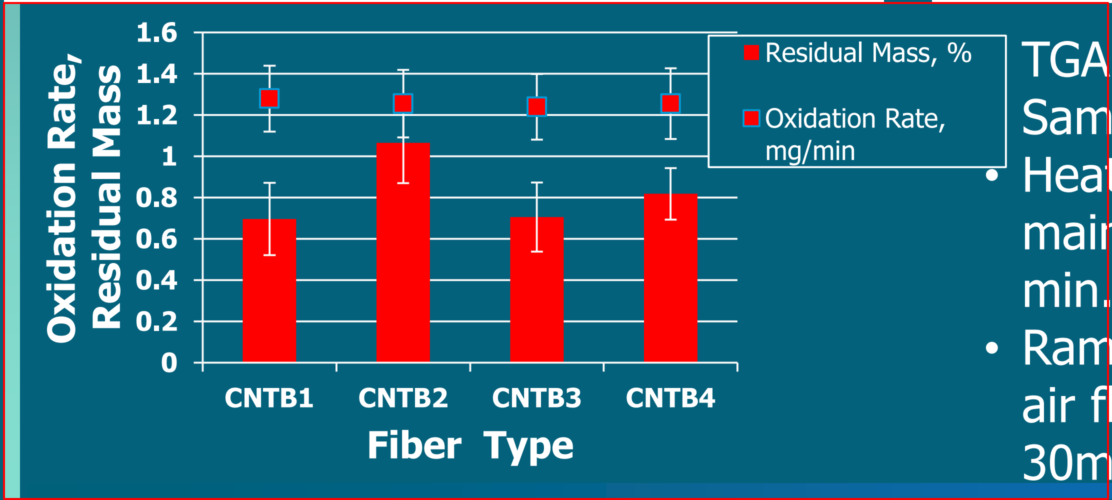
Effect of POSS Coating



CNT Characterization using TGA







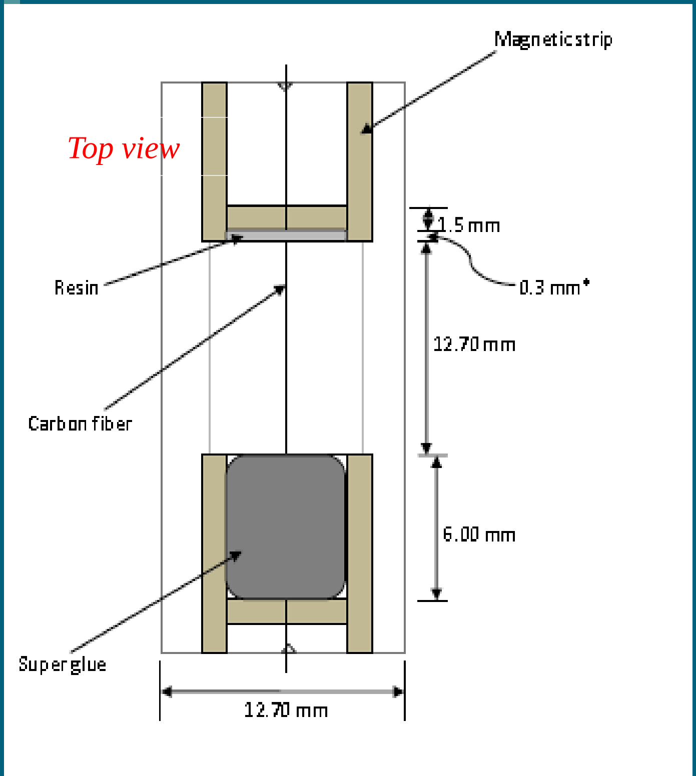
TGA Q50 ceramic pan (500μL)

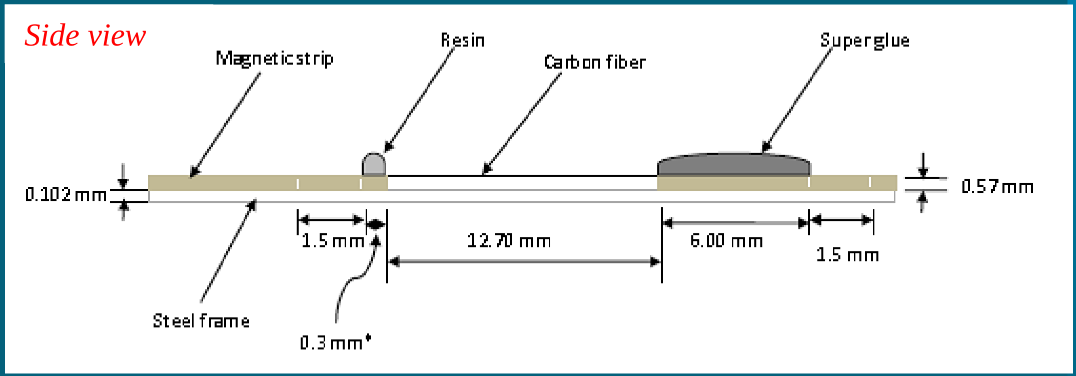
Sample: 18-20mg

- Heated up to 100°C and maintained at this set point for 30 min.
- Ramped to 800 °C at 2°C/min and air flow rate was maintained at 30mL/min

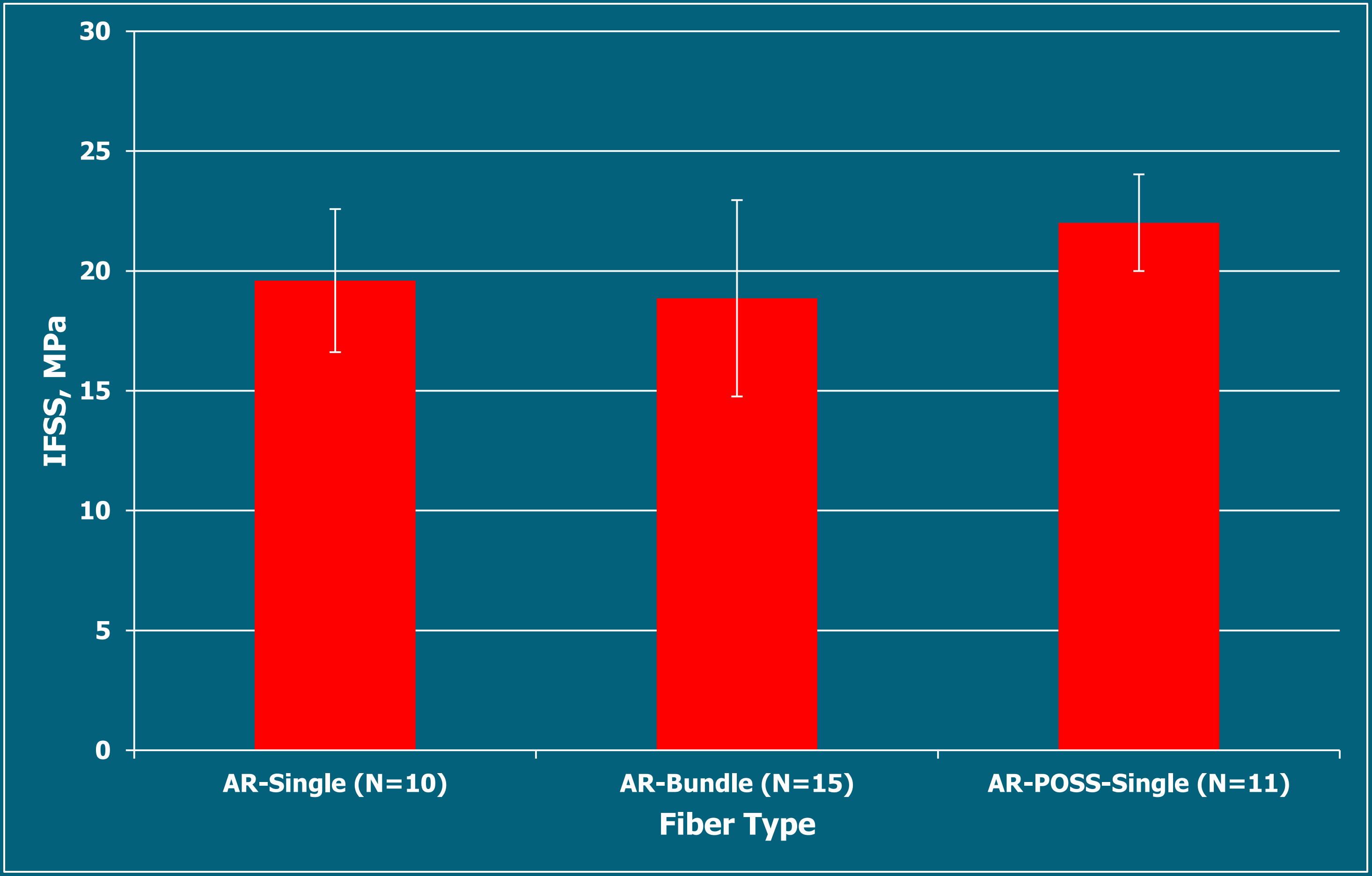
Measurement of Interfacial Properties

- Fiber: AR, TT, CNTB1, CNTB2, CNTB3 and CNTB4
- Resin : Araldite LY-1556/Aradur 2469 (curing agent (100:35)
- Force is ramped at **0.2N/min to 10N**
- The frame window size (gauge length) was 12.70mm

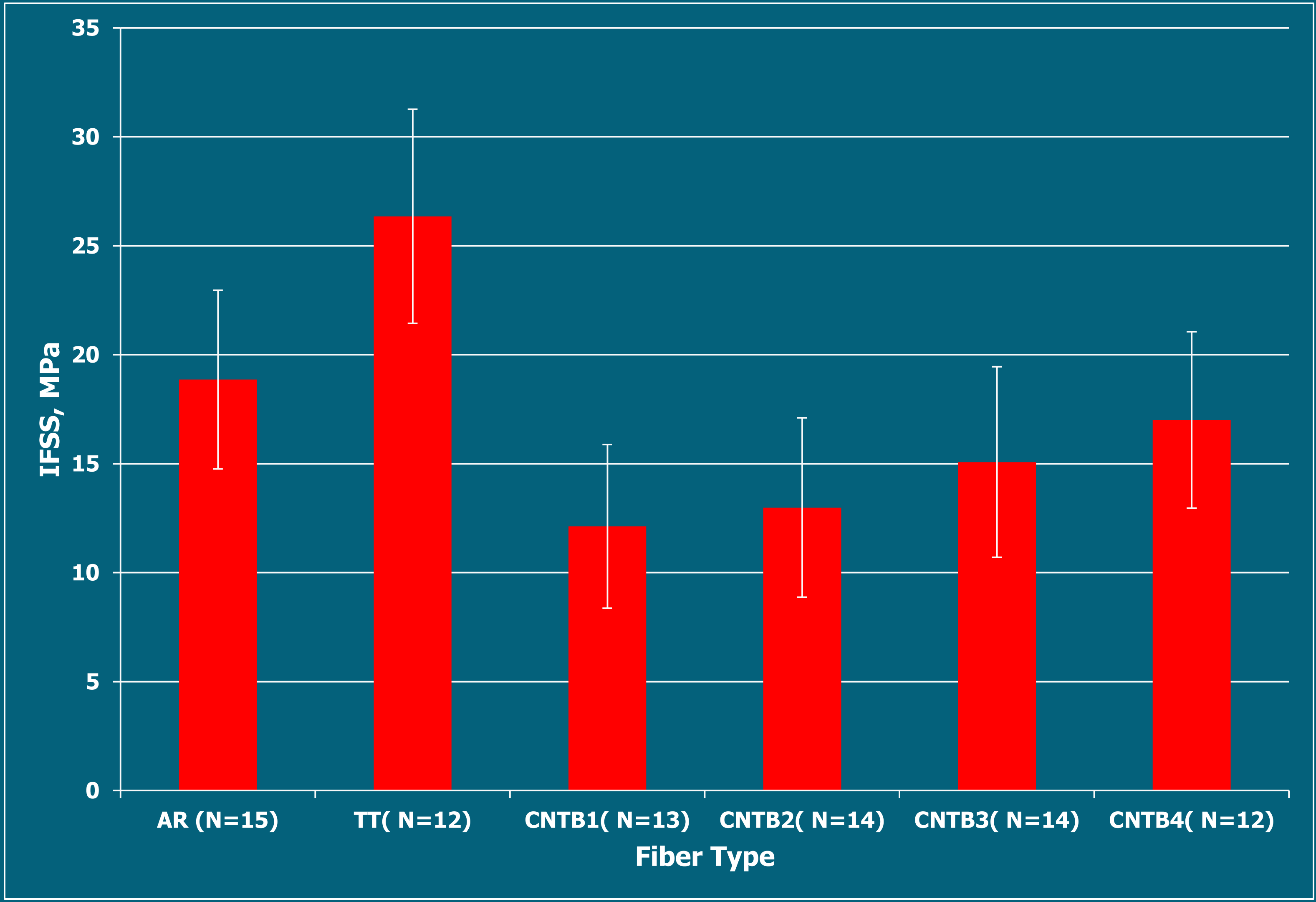




Single Fiber vs. Fiber Bundle



Effect of CNTs on Interfacial Properties



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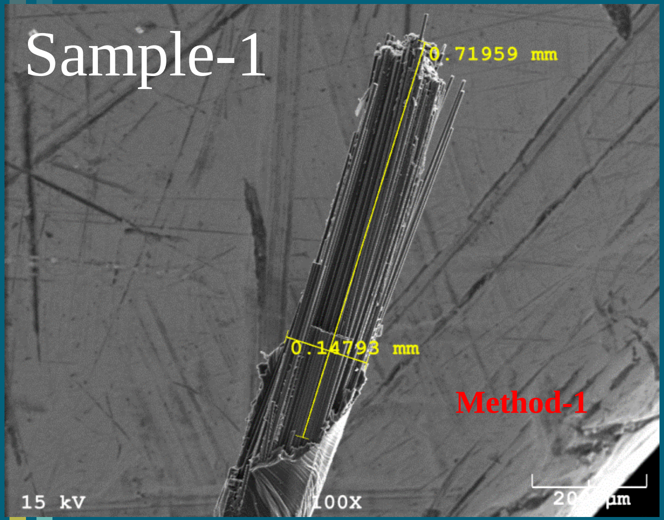
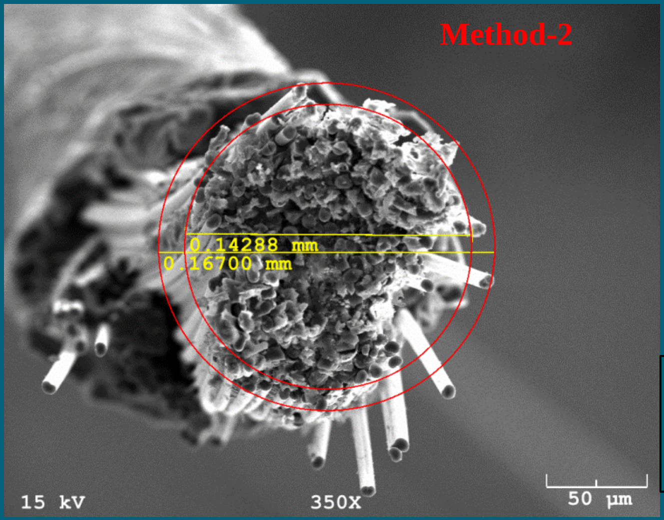
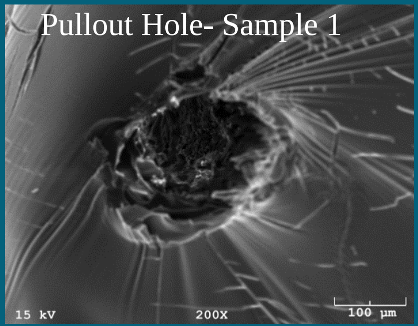
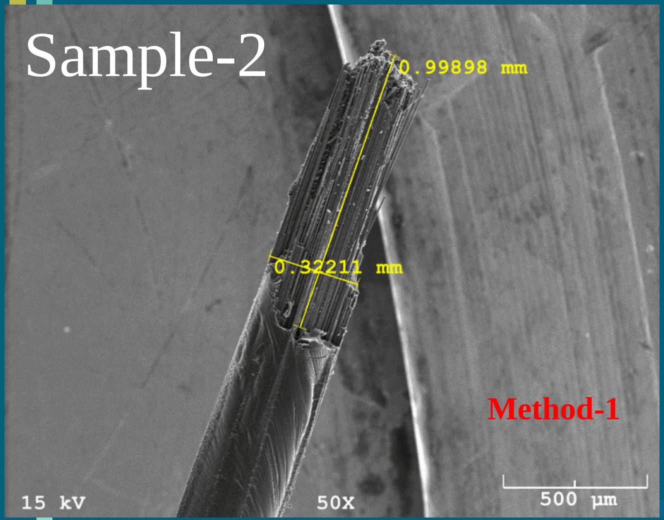
Diameter and Embedded Length Measurement

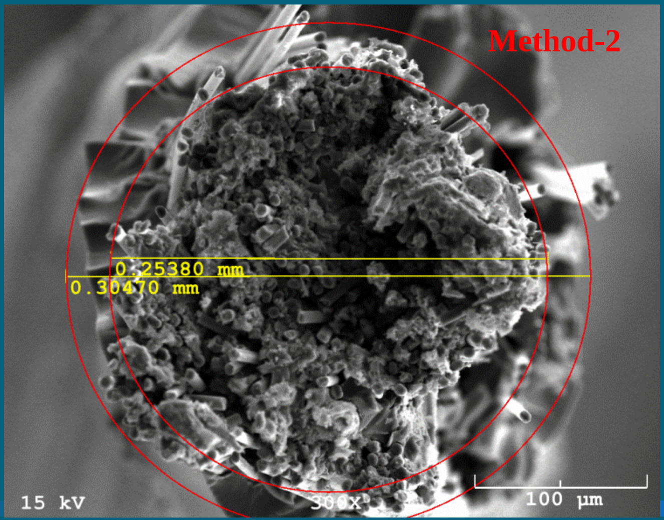


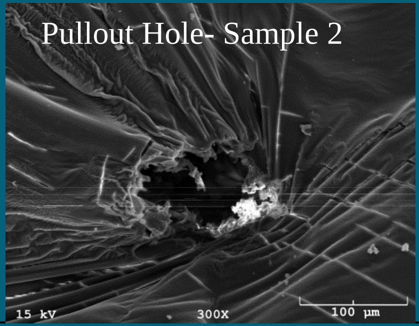




Sample#1 Diameter:
Method 1= 0.14793 mm
Method 2= 0.15494 mm





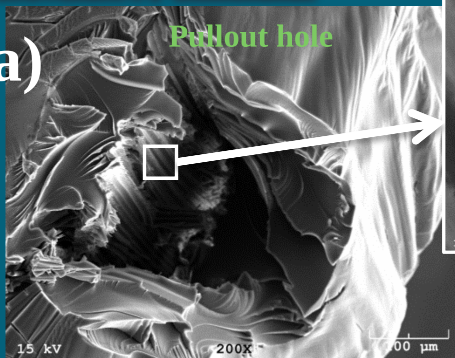


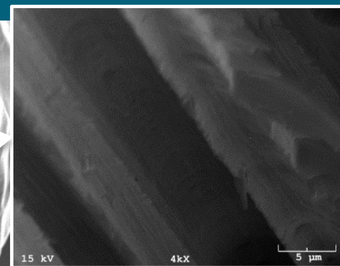
Sample#2 Diameter:
Method 1= 0.32211 mm
Method 2= 0.27925 mm

SEM Micrographs showing the pullout hole and the embedded bundle fiber length:

(a) AR (b) TT and (c) CNTF

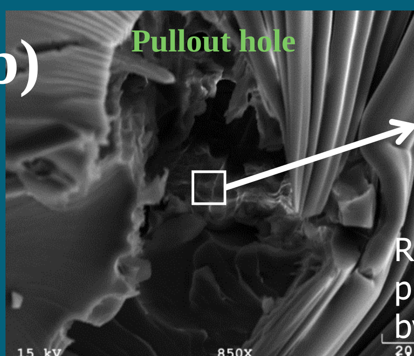
(a)

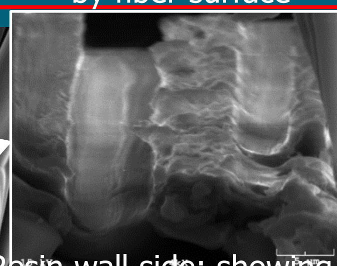




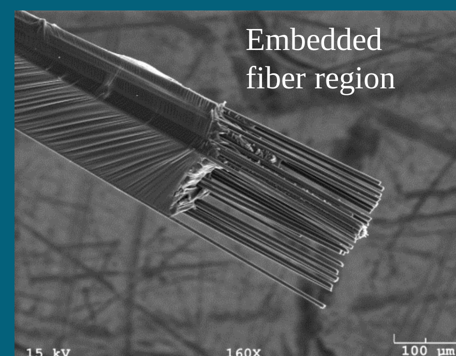
Resin wall side: showing strips created by fiber surface

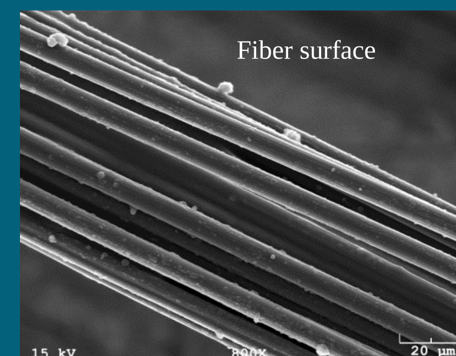
(b)





Resin wall side: showing pronounced strips created by fiber surface (due to thermal treatment)





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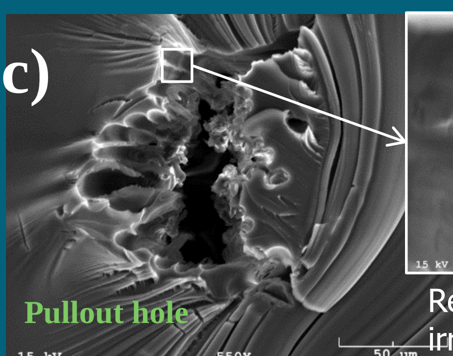
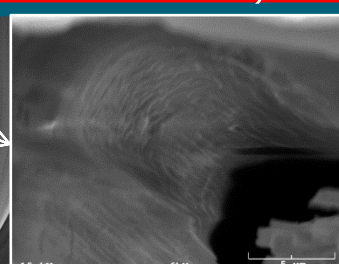
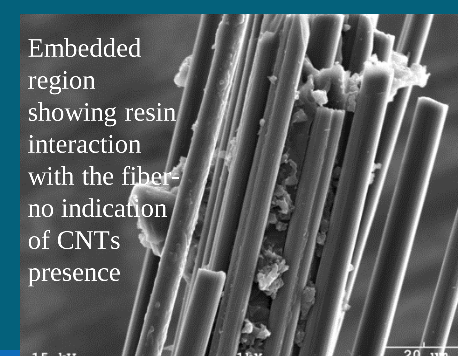
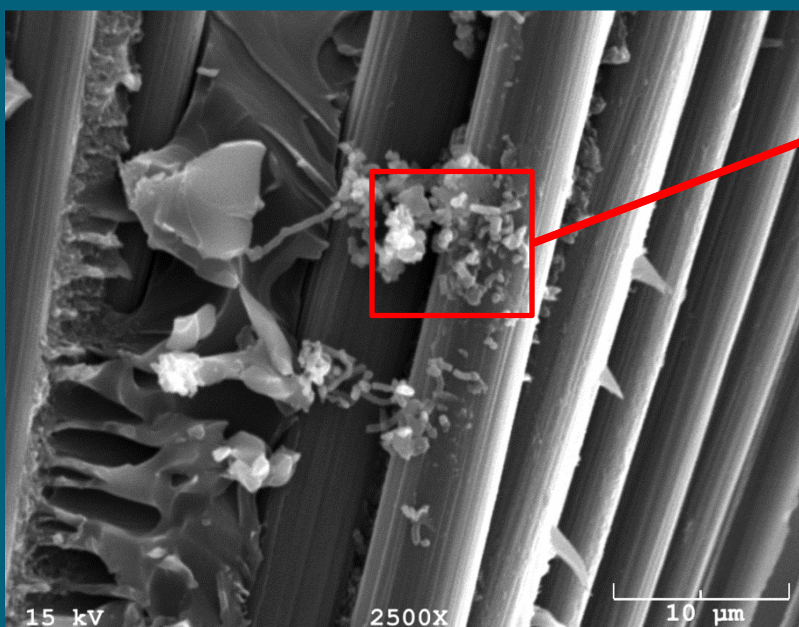


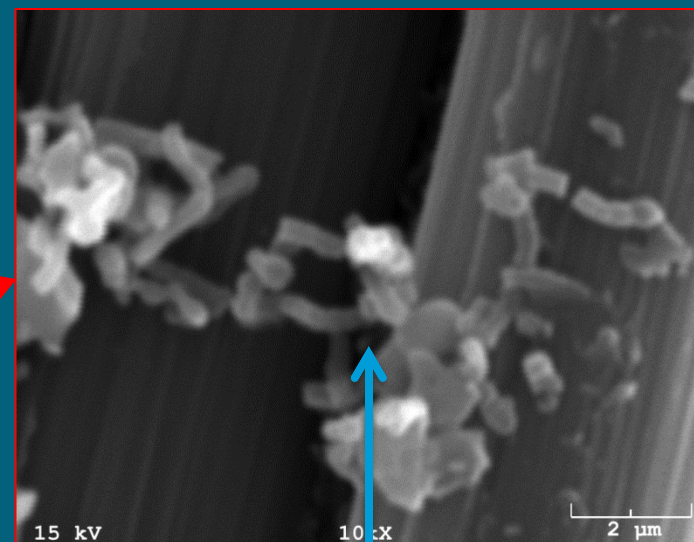


Resin wall side: showing irregular surface created by fiber surface



SEM Investigation of Pullout Fiber Bundle

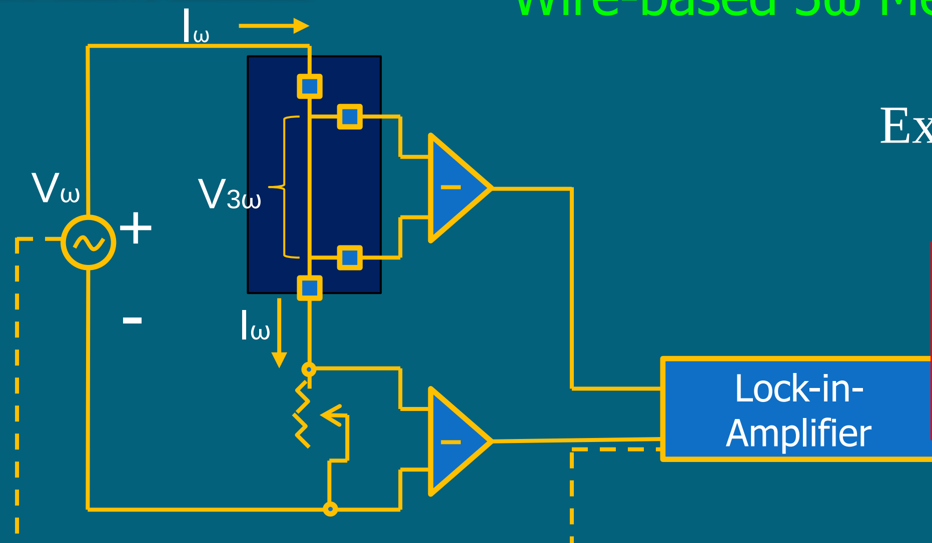




Remains of CNTs on the fiber after the pullout

Thermal Conductivity Measurement

Wire-based 3ω Method



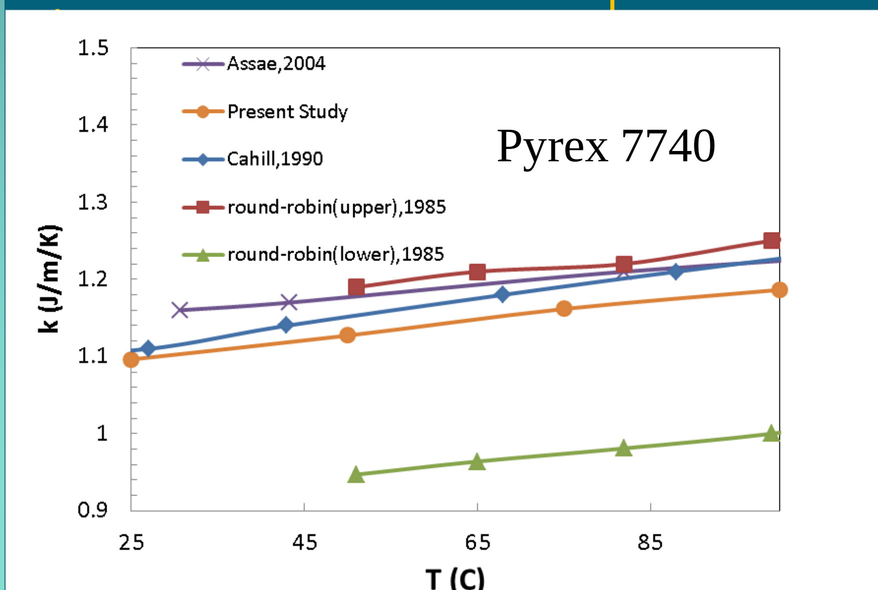
Experimental thermal impedance

$$T = QZ$$

$$Z = -\frac{4R^2bL}{V^3{}_{rms}\,\frac{\partial R}{\partial T}}V_{3\omega\_rms}$$

Analytical thermal impedance

$$\hat{Z} = \int_{4\pi}^{4\pi} \frac{\sin(\chi)}{\chi^2} \frac{-b}{k_y\sqrt{\frac{k_x}{k_y}\chi^2 + \frac{i4\pi f b^2}{\alpha}}} d\chi$$



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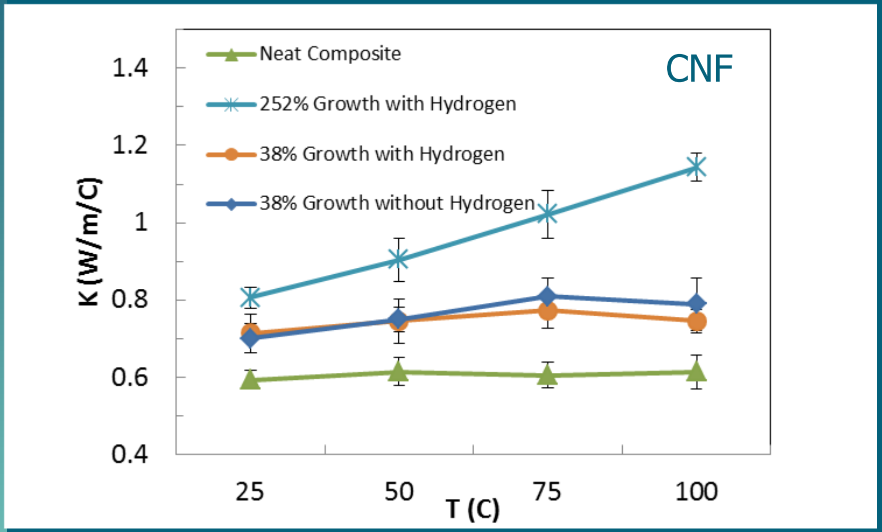
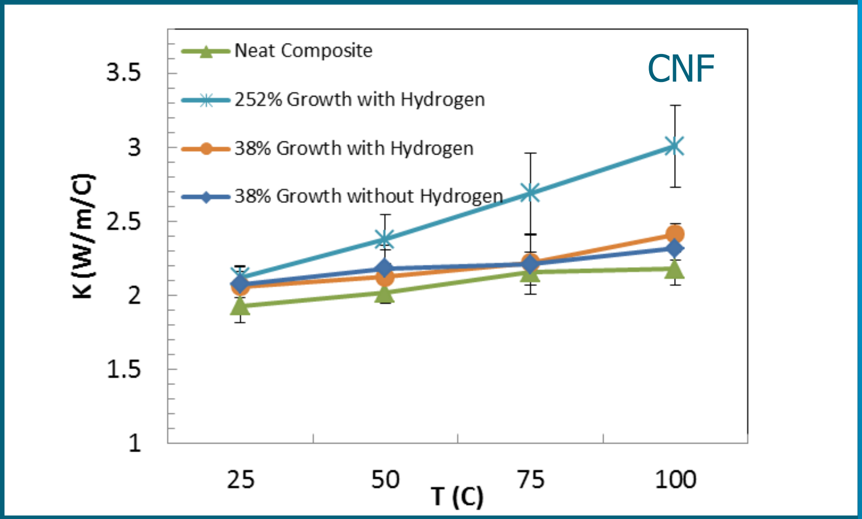
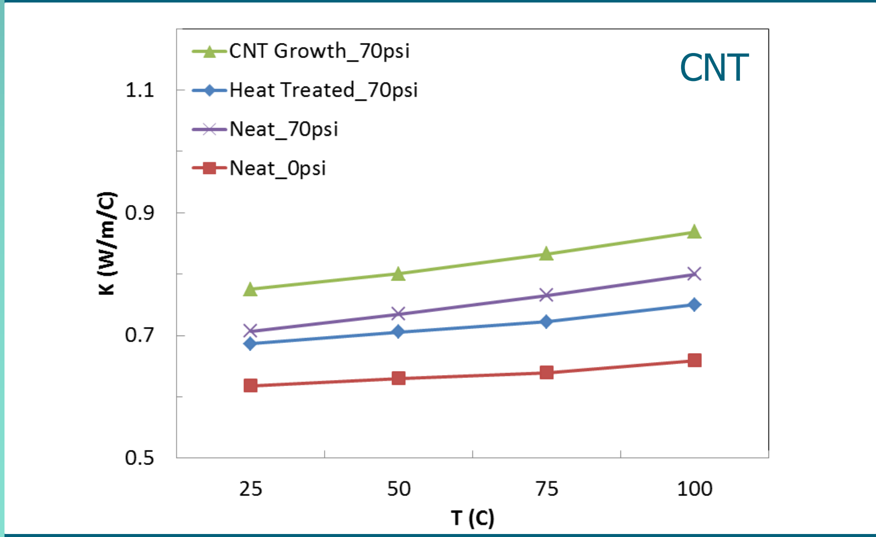
Thermal Conductivity of Composites

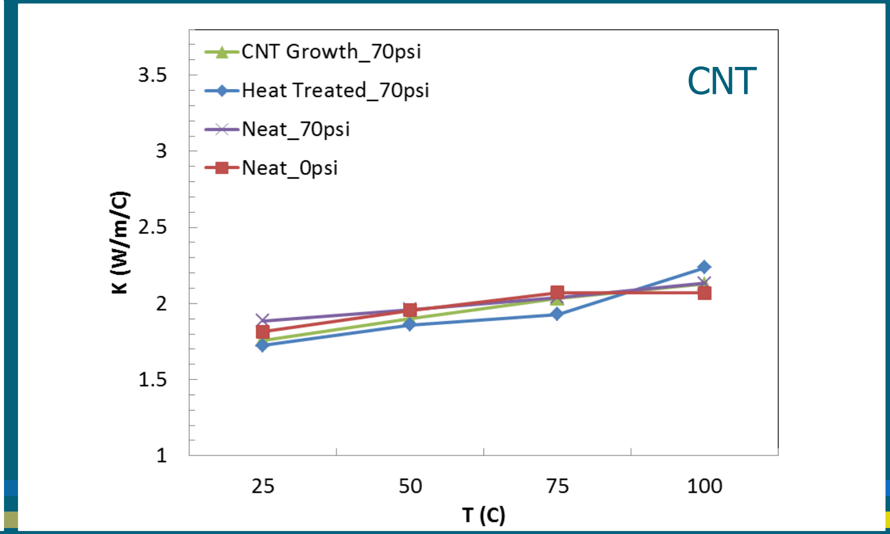




Through-thickness direction

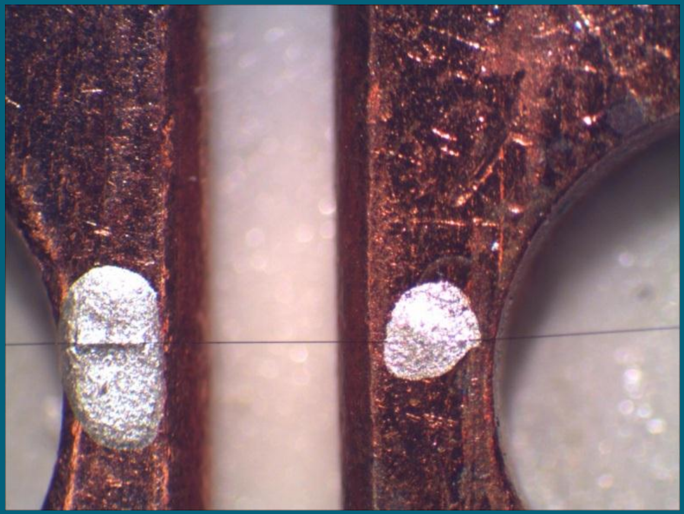
In-plane direction



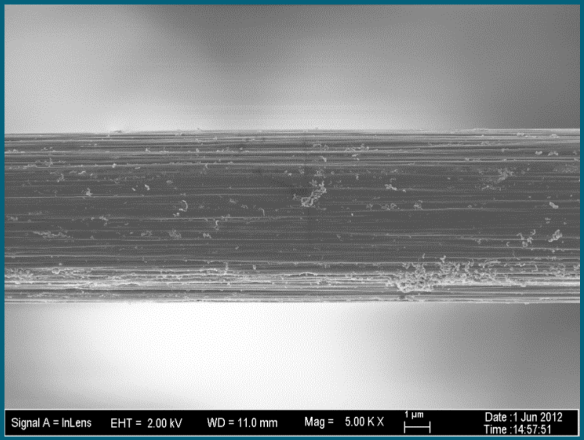


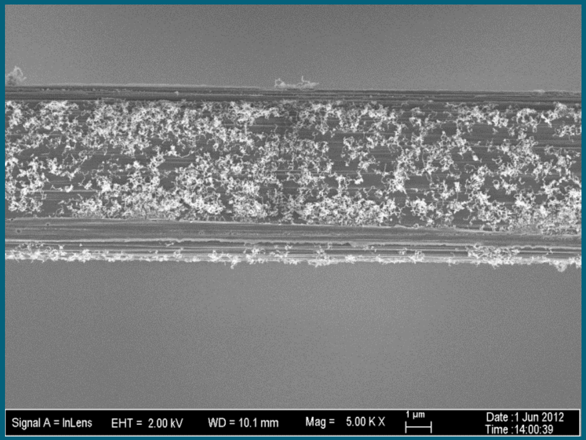
Thermal Conductivity of Single fiber

- Lu's model (Lu *et al* 2001)



	K (W/mK)
Neat	14.4
Heat Treated	15.5
CNT Growth	18.1



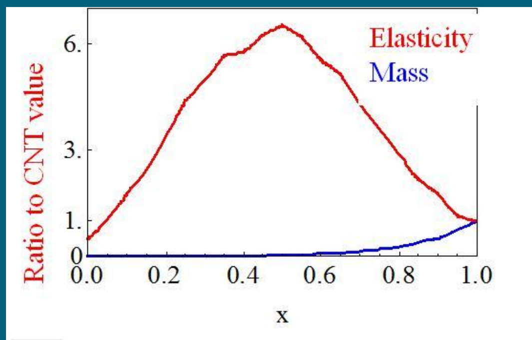


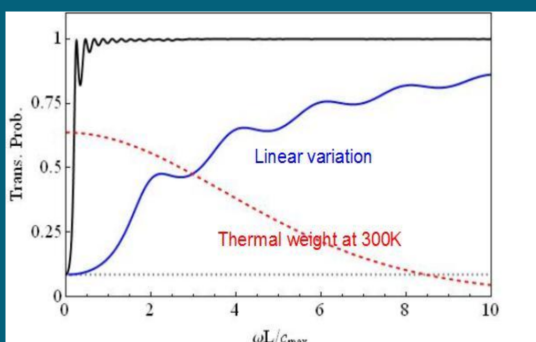
TC =15.03 W/mK

TC = 21.06 W/mK

Effect of CNT Interface on TC

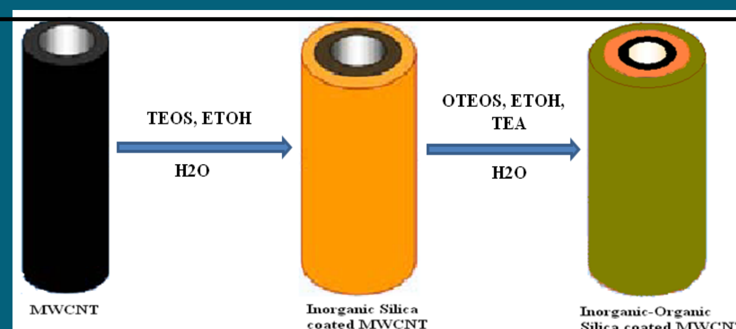
Functionalize the end of 1-D CNT structure with molecular chains of varying stiffness and mass density

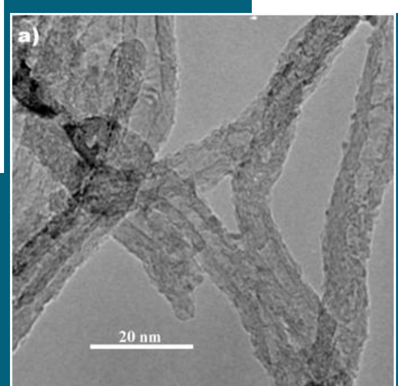




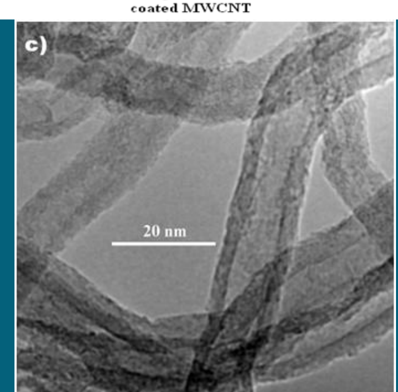
An interface with the optimal variation of elasticity and mass as a function of position (top) transmits nearly all phonons (black line, bottom) better than either an abrupt interface (dotted line) or a linear variation (blue line)

Unit (nm)	Pristine	One-layer coating	Two-layer coating
Avg. Diameter	9.1 ± 3.1	10.4 ± 3.8	11.7 ± 4.2
Maximum	20.0	24.5	27.6
Minimum	3.0	4.2	4.8

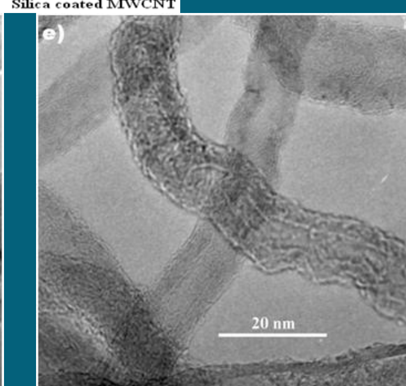




Pristine MWCNTs

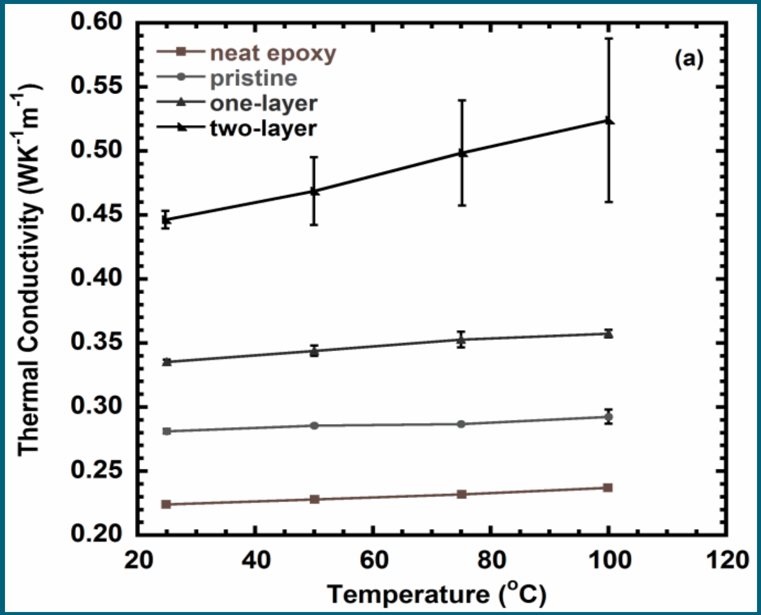


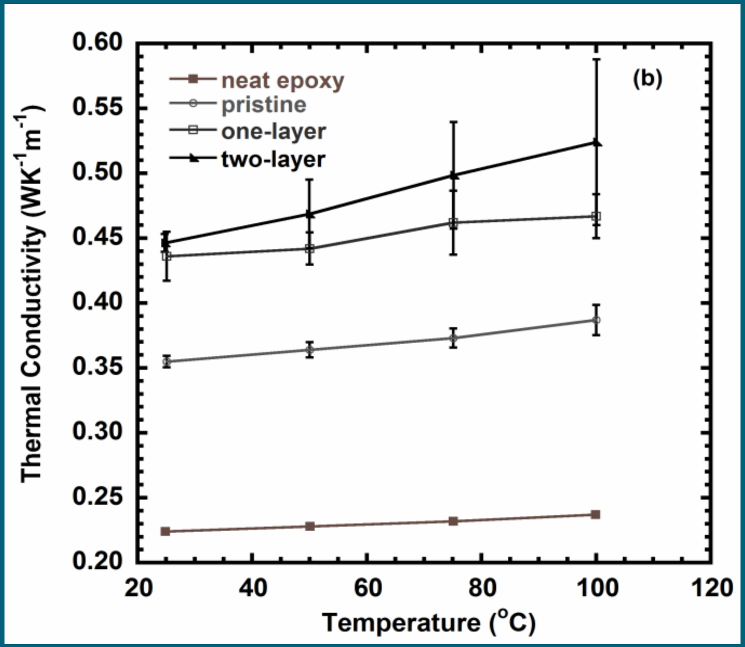
One-layer coating



Two-layer coating

Effect of CNT Interface on TC



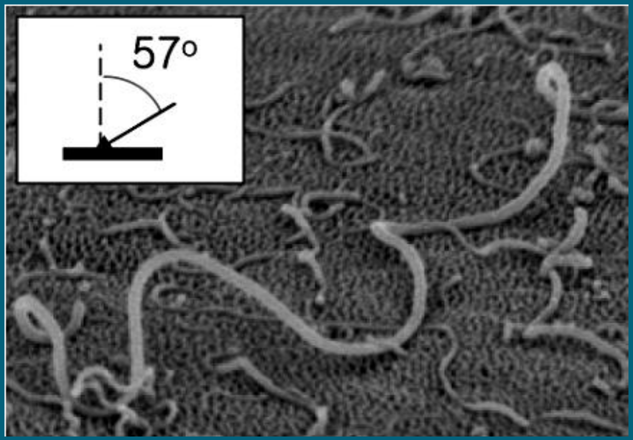


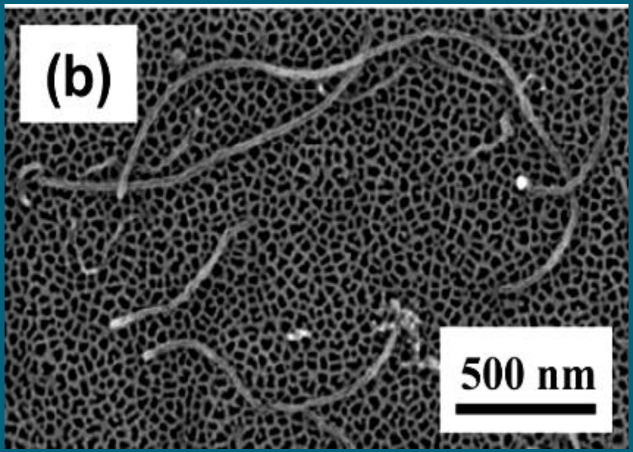
Amount of pristine, one-layer and two-layer of MWNTs is 0.5, 0.83 and 1.0 wt%, respectively, corresponding to 0.5wt% nanotube on nanotube basis

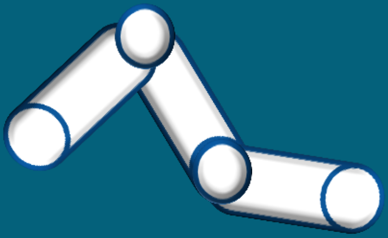
Amount of filler is 1.0 wt% for all three types of MWNTs on a total filler basis

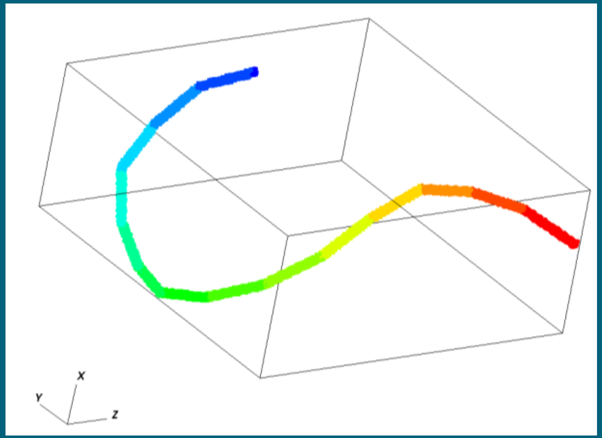
Mesoscale Modeling of Thermal Conductivity (Monte-Carlo)

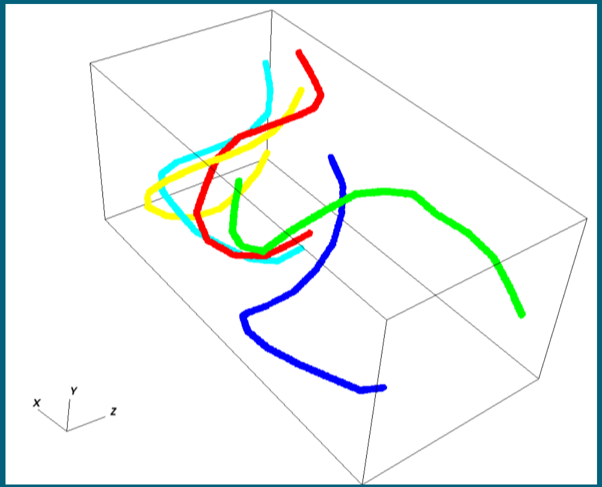
Worm-like CNTs in 3D











SEM of MWCNTs on ceramic filter.
Lee *et al., JPCC 111(51) 2007*

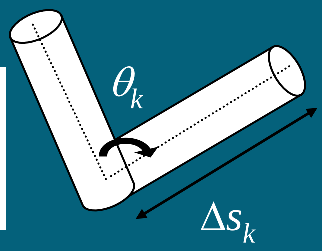
Configuration of CNTs inside the computational box:
random placement and random oriented

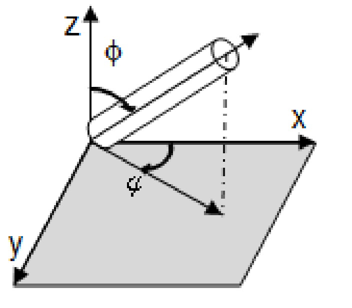
Modeling of Thermal Conductivity

Persistence length, L_p:

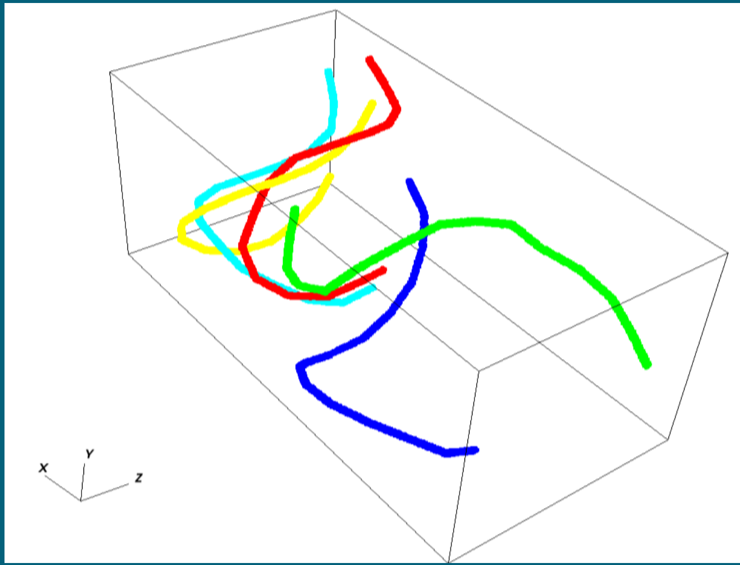
$$L_p = \frac{L^2}{(N-1)^2 \pi^2 \operatorname{var}(a_n)}$$

$$a_n \cong \sqrt{\frac{2}{L}} \sum_{k=1}^{N} \theta_k \Delta s_k \cos\left(\frac{n\pi}{L} s_k^{mid}\right), n = 1, \ldots, N-1$$

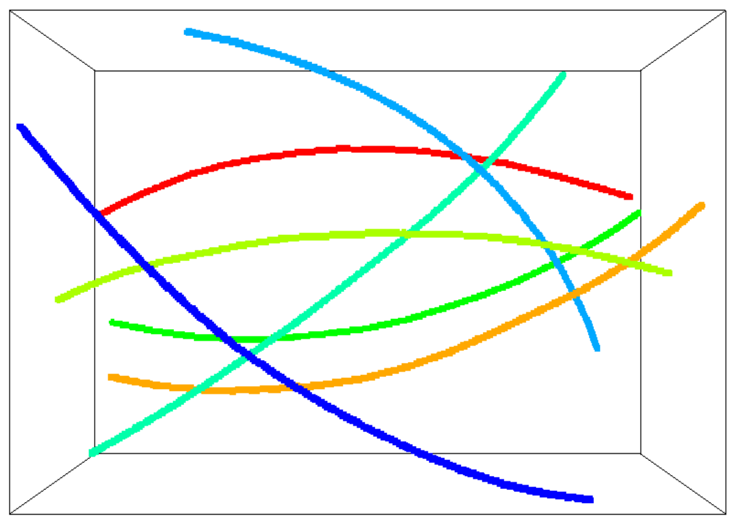




Gittes F. *et al.*, J. Cell Biology 1993, 120, 923-934



$L_p < L$



$L_p \approx L$

Modeling of Thermal Conductivity

L_p of pristine and 2-layer coating MWCNTs

Sample	pristine	2-layer coating
Average L_p (nm)	294.25	273.46
Stdev (nm)	174.90	195.21

L_p MWCNTs ≈ 271nm, Lee *et al., JPCC 111(51) 2007*

=> The SiO_2 coating did not alter the persistence length of MWCNTs

Modeling of Thermal Conductivity Monte-Carlo method

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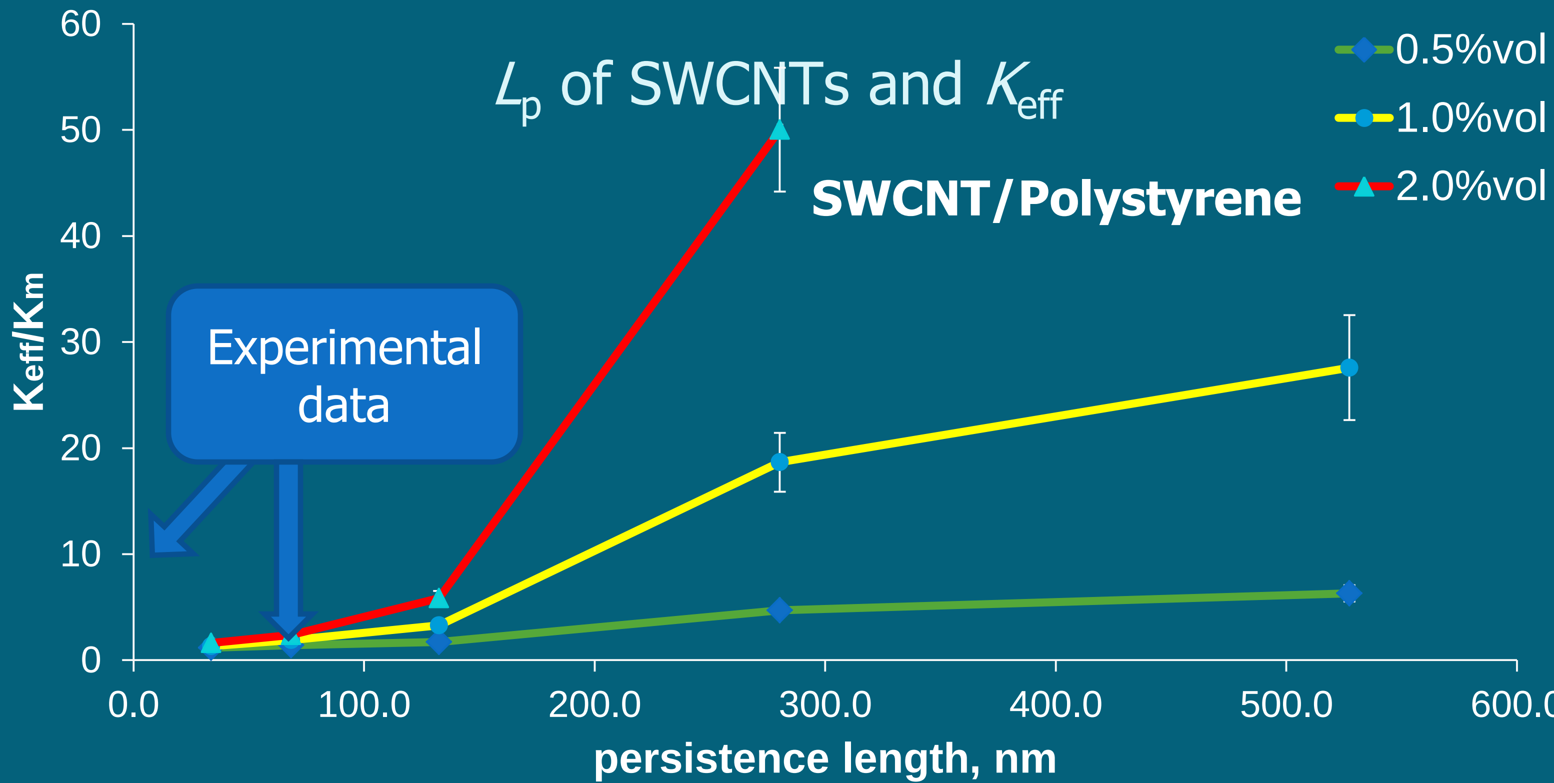

***Average L_p* (nm)**	33.6	68.4	132.6	280.3	527.4
Critical angle (degree)	90	43.2	21.6	10.8	5.4

Effect of End-to-End Length

Average L_e (nm)	155	218	321	289	149
Average L_p (nm)	30	55	179	398	812
$L_{contour}$ (nm)	750	600	450	300	150
Average K_{eff}/K_m	1.79	2.74	6.94	2.96	1.14
Var(K_{eff}/K_m)	0.42	0.39	1.09	0.41	0.03

$L_{end\text{-}to\text{-}end} = f(L,L_p)$ is the key nanotube length that affects the effective thermal conductivity (K_{eff}).

Bui K. et al., 2012 submitted to J. Numerical Heat Transfer

Summary

- Uniform growth of CNFs and CNTs was achieved on large carbon fabric
- Catalyst loading, reaction time, catalyst deposition, and hydrogen dilution were found to affect the growth morphology
- Carbon fiber with CNT showed slight increase in tensile properties and thermal conductivity at both fiber and composite levels
- However, slight decrease in interfacial properties of CNT-grown fibers were due to non-uniform growth
- Step gradient interface modification of CNT showed slight improvement in thermal conductivity
- Effect of CNT wavyness seemed to affect thermal conductivity of nanocomposites

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